EFFECT OF CLUSTER FORMATION ON THE VISCOSITY OF DENSE GASES

ARUN K. PAL AND A. K. BARUA

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA

(*Received September 15, 1966*)

ABSTRACT. The effect of dimerization on the viscosity of dense gases has been calculated for the rigid sphere molecules by utilising an extension of the Enskog theory for dense gases. This treatment as distinguished from the earlier ones, takes into consideration the effect of dimerization on the collisional transfer term. Sample calculations made for Argon show that the contribution of dimerization to the viscosity is negative at low pressure and it becomes positive with the increase of pressure.

INTRODUCTION

For the calculation of the transport properties of dense gases it is necessary to consider the collision transfer (Chapman and Cowling, 1952) in addition to the transfer by molecular interaction. Enskog (Chapman and Cowling, 1952) long ago, first formulated a theory for the dense gases by considering the molecules to be rigid spheres. The advantage of this assumption is that the probability of multiple encounters become negligible. It has subsequently been found (Hirschfelder, Curtiss and Bird, 1954) that the Enskog theory can represent the transport properties of dense gases only approximately. Several attempts have been made to improve the Enskog theory by introducing semi-empririal corrections. Recently, Snider and Curtiss (1958, 1960) and Snider and McCourt (1963) have made a significant advance in the theory of dense gases. They have modified the Boltzmann equation which is an approximation to the series development of Bogolubov (1946) and Hollinger and Curtiss (1960). Curtiss, McElroy and Hoffman (1964) have used numerical methods to consider the effect of three body collisions on the first density term by a generalization of the Enskog rigid sphere expression.

Another factor which is of importance in the dense gases is the formation of clusters or bound molecules. As has already been pointed out by Das Gupta and Barua (1965) at sufficiently high pressures the gas should be treated as a mixture of monomers and j-mers. Stogryn and Hirschfelder (1941) have considered the formation of dimers in non-polar gases on realistic potential models. The effect of dimerization on the transfer by interaction has been considered by them. This treatment has recently been improved by Kim and Ross (1965) who considered the presence of quasi-dimers. These treatments are valid only for the initial pressure dependence. For higher densities it is necessary to consider the change

in the collisional transfer term due to cluster formation. At not too high pressures it is sufficient to consider dimerization only. In this paper a start has been made in this direction. We have made a sample calculation of the effect of dimerization on the viscosity of argon on the rigid sphere model. The results will show if the contribution of dimerization is of significant magnitude.

METHOD OF CALCULATION

The co-efficient of viscosity of a dense gas η_p on the Enskog theory may be expressed as (Chapman and Cowling, 1952)

$$\eta_p = \eta_0 b\rho \left[\frac{1}{b\rho\chi} + \frac{4}{5} + 0.7614 b\rho\chi \right], \quad \ldots (1)$$

where η_0 is the zero-pressure viscosity, ρ the density, $b\rho = \frac{2}{3}\pi n\sigma^3$, σ being the collision diameter. The quantity χ is given by,

$$\chi = 1 + \tfrac{5}{8}\rho b + 0.2869\rho^2 b^2 + \ldots, \quad \ldots (2)$$

The Enskog theory for a pure dense gas has been extended to the case of a binary mixture (Chapman and Cowling, 1952) and the viscosity for such a mixture may be written as,

$$\begin{aligned}[\eta_p]_{mix} = {} & \tfrac{5}{2} kT \,[b_{-1\,-1} n_{12} \,(1 + \tfrac{2}{5} b_1\rho_1\chi_1 + \tfrac{4}{5} M_2 b'_2 \rho_2 \chi_{12})^2 \\ & - 2b_{1-1}\,(1 + \tfrac{2}{5} b_1\rho_1\chi_1 + \tfrac{4}{5} M_2 b'_2\rho_2\chi_{12})(1 + \tfrac{2}{5} b_2\rho_2\chi_2 + \tfrac{4}{5} M_1 b'_1\rho_1\chi_{12}) \\ & + b_{11} n_{21}(1 + \tfrac{2}{5} b_2\rho_2\chi_2 + \tfrac{4}{5} M_1 b'_1\rho_1\chi_{12})^2]/[\chi_{12}(b_{11}\, b_{-1-1} - b^2_{1-1}) \\ & + \tfrac{4}{15}(\pi kT)^{\frac{1}{2}} \{m_1^{\frac{1}{2}} n_1^2 \chi_1 \sigma_1^4 + 2(2m_0 M_1 M_2)^{\frac{1}{2}} n_1 n_2 \chi_{12}\sigma_{12}^4 + m_2^{\frac{1}{2}} n_2^2 \chi_2 \sigma_2^4\}], \quad \ldots (3)\end{aligned}$$

In this formula,

$$\chi_1 = 1 + \frac{5}{12}\pi n_1\sigma_1^3 + \frac{\pi}{12} n_2(\sigma_1^3 + 16\sigma_{12}^3 - 12\sigma_{12}^2\sigma_1) + \ldots \quad \ldots (4)$$

$$\chi_{12} = 1 + \frac{\pi}{12} n_1\sigma_1^3(8 - 3\sigma_1/\sigma_{12}) + \frac{\pi}{12} n_2\sigma_2^3(8 - 3\sigma_2/\sigma_{12}) + \ldots \quad \ldots (5)$$

with a corresponding equation for χ_2. The subscripts 1, 2 stand for the components, 1, 2 respectively. We have also the following relations viz :

$$b_{11} = b'_{11} + n_{12}\chi_1 b''_{11}/\chi_{12}, \quad \ldots (6)$$

$$b_{-1-1} = b'_{-1-1} + n_{21}\chi_2 b''_{-1-1}/\chi_{12}, \quad \ldots (7)$$

$$b_{1-1} = -5kT(\tfrac{2}{5} - A)/E, \quad \ldots (8)$$

$$b'_{11} = 5kT(\tfrac{2}{5} + M_2 A/M_1)/E, \quad \ldots (9)$$

$$b''_{11} = 5kT/2[\eta_1]_1, \quad \ldots (10)$$

The constant A depends on the ratio of the collision integrals.

The percentage of dimers at any particular temperature and pressure may be obtained from the equilibrium constant for dimerization,

$$K_2(T) = -(B_b+B_m)n/V, \quad \ldots (11)$$

$$= n_2V/{n_1}^2, \quad \ldots (12)$$

$B_b(T)$ and $B_m(T)$ being the constribution of the bound double molecules and metastably bound molecules which have been calculated on the Lennard-Jones (12:6) model by Stogryn and Hirschfelder (1959). n_1, n_2 are respectively the number densities of monomers and dimers.

In order to obtain σ_2 it is necessary to calculate the viscosity of dimers. On the Lennard-Jones (12 :6) model it has been shown by Stogryn and Hirschfelder (1959),

$$\frac{\sigma_{12}}{\sigma_1} = 1.03; \quad \frac{\epsilon_{12}}{\epsilon_1} = 1.32 \quad \ldots (13)$$

We have also the combination rules

$$\sigma_{12} = \tfrac{1}{2}(\sigma_1+\sigma_2) \; ; \quad \epsilon_{12} = (\epsilon_1 \cdot \epsilon_2)^{\frac{1}{2}} \quad \ldots (14)$$

Thus by knowing σ_1, ϵ_1, σ_{12} and ϵ_{12} it is possible to calculate σ_2 and ϵ_2 from Eqs. (13) and (14). With these force constants for the dimers on the Lennard-Jones (12:6) model the viscosity values were calculated from the expression

$$\eta \times 10^7 = 266.93 \; \frac{\sqrt{MT}}{\sigma^2 \Omega^{*(2,2)}(T^*)} \quad \ldots (15)$$

where $\Omega^{*(2,2)}(T^*)$ is a reduced collision integral which has been tabulated as a function of $T^* = kT/\epsilon$. From the values of viscosity at any temperature as obtained from Eq. (15) σ_2 was calculated on the rigid sphere model from the expression,

$$\eta \times 10^7 = 266.93 \; \frac{\sqrt{MT}}{\sigma^2}, \quad \ldots (16)$$

For sample calculation of the effect of dimerization we have chosen the viscosity data of argon at 25°C (Michels, Botzen and Schuurman, 1954) The results obtained are shown in the Table I. It may be seen from the table that at lower pressures the effect of dimerization is to lower the viscosity which is in agreement with the results obtained by Barua and Das Gupta (1963) for steam and ammonia. However, at higher pressures the dimerization makes a positive contribution to viscosity. This may be due to the effect of dimers on the collisional transfer which overshadows the effect on the transfer by interaction, which is evident from the columns 4-6 of Table I. We have not made the calculations at higher pressures which will need the consideration of larger clusters. In fact at the highest pres-

sures considered by us, the positive contribution becomes less which is probably due to the importance of larger clusters at that pressure. As our main purpose in this paper is to find the effect of cluster formation on the rigid sphere model, we have not compared with the experimental viscosity data. In a subsequent paper we propose to make more realistic calculations.

Pressure (Atm.)	Density (g./cc.)	%of Dimers	$[\eta_p]\times 10^4$ mix calculated from eqn. (13) Poise	$\eta_p\times 10^4$ calculated from eqn. (1) Poise	$(\eta_{mix}-\eta_{cal})\times 10^4$ in %
65.9	0.1115	6.41	2.327	2.380	−2.23
105.4	0.1806	9.65	2.540	2.535	0.72
175.2	0.3016	14.50	3.055	2.985	2.35
351.2	0.5558	21.92	5.171	4.955	4.44
465.5	0.6728	24.90	6.754	6.505	3.80

The authors are grateful to Prof. B. N. Srivastava for his kind interest and encouragement.

REFERENCES

Barua, A. K. and Dasgupta, A., 1963, *Trans. Faraday Soc.*, **59**, 2243.

Bogolubov, N. N., 1946, *J. Phys. (U.S.S.R.)*, **10**, 265.

Chapman, S., and Cowling, T. G., 1952, *The Mathematical Theory of Non-Uniform Gases*, Oxford University Press.

Curtiss, C. F., McElroy, M. B., and Hoffman, D. K., 1964, *WIS TC* 1-46, May.

Dasgupta, A., and Barua, A. K., 1965, *J. Chem. Phys.*, **42**, 2849.

Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., 1954, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, N. Y.,

Hollinger, H. B., and Curtiss, C. F., 1960, *J. Chem. Phys.*, **33**, 1386.

Kim, S. K., and Ross, J., 1965, *J. Chem. Phys*, **42**, 263.

Michels, A., Botzens, A., and Schuurman, W., 1954, *Physica*, **20**, 1141.

Snider, R. F., and Curtiss, C. F., 1958, *Phys. Fluids*, **1**, 122.

———, 1960, *Phys Fluids*, **3**, 903.

Snider, R. F., and McCourt, F. R., 1963, *Phys. Fluids*, **6**, 1029.

Stogryn, D. E., and Hirschfelder, J. O., 1959, *J. Chem. Phys.*, **31**, 1531.